Band gap grading in Cu(In,Ga)Se$_2$ solar cells

M. Gloeckler and J. R. Sites

Department of Physics

Colorado State University

Fort Collins, CO 80523-1875

Abstract

The quaternary system Cu(In,Ga)Se$_2$ (CIGS) allows the band gap of the semiconductor to be adjusted over a range of $1.04 - 1.67\,\text{eV}$. Using a non-uniform Ga/In ratio throughout the film thickness, additional fields can be built into p-type CIGS-based solar cells, and some researchers have asserted that these fields can enhance performance. The experimental evidence that grading improves device performance, however, has not been compelling, mostly because the addition of Ga itself improves device performance and hence a consistent separation of the grading benefit has not always been achieved. Numerical modeling tools are used in this contribution to show that (1) there can be a beneficial effect of grading, (2) in standard thickness CIGS cells the benefit is smaller than commonly believed, (3) there is also the strong possibility of reduced rather than of increased device performance, and (4) thin-absorber cells derive more substantial benefit.

Key words: A. chalcogenides, A. thin films

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1 Introduction

Record conversion efficiencies of CdS/CIGS thin-film solar cells are approaching 20% [1]. The absorber layers used in these cells are deposited by the three-stage process [2], which leads to non-uniform Ga/In composition versus absorber depth. Other methods commonly used, such as co-evaporation, allow the engineering of Ga/In profiles by varying the element fluxes during deposition. The effects of these non-uniform Ga/In compositions in $CuIn_{1-x}Ga_xSe_2$ have been broadly investigated by simulations and experiments. Simulations have predicted: (1) small (<0.5%) to moderate (<1%) improvements in efficiency with an increase in x towards the back contact, "back grading" [3–7], (2) small to large (>2%) improvements with an increase in x towards the junction, "front grading" [4–8] (3) small to large improvements with an increase in x towards front and back and a minimum band-gap in between, "double grading" [3–6,9,10]. Interpretation of experiments agree reasonably well with these results in showing moderate improvements due to back grading [7,11–13], moderate improvements due to front grading [7] and large improvements (>3%) due to double grading [9–11]. Often however, there is a wide range of results available when simulation parameters or experimental conditions were varied, such that back [4,7,11], front [4,7,12], and double grading [10] have also been observed to reduce efficiency.

Substitution of Ga for In in Cu(In,Ga)Se$_2$ enlarges the band gap from 1.04 to 1.67 eV, with the change occuring primarily in the conduction band [14]. Simulated device efficiency η and open-circuit voltage V_{oc} are shown in Fig. 1 for solar cells with uniform band-gap energies (details of the model are discussed below). Typical high-efficiency devices have minimum band gaps of

1.1 to 1.2 eV. Addition of a Ga/In grading to an absorber with a minimum band gap $E_{min} < 1.4$ eV *may increase its performance due to either the grading benefit or the increase in average Ga content* (higher average band gap in Fig. 1). In fact, Dullweber [7] observed a close correlation between the average Ga-content and the device performance, independent of the Ga distribution. Except for references [4,7,13], uniform band-gaps equal to the graded band-gap minimum (1.04 eV "CIS", in most cases) are used for comparison to determine the grading benefit. This unfortunate selection of the reference performance, results in overestimates of efficiency gains attributed to the grading benefit, especially for front and double grading structures where the band gap increases in high recombination regions. In Refs. [4] and [7] an average band-gap is used for comparison, and in Ref. [13] the results are normalized to the optical band-gap.

To eliminate the grading vs. average band-gap complication, graded device structures in this article are compared with ungraded devices with the same open-circuit voltages. Because of the monotonic increase of the open-circuit voltage with band gap, this choice establishes an objective and absolute criteria for grading benefits, independent of changes in average Ga composition. The alternative comparison to the effective optical band-gap used in Ref. [13] would yield similar results.

2   Device Model

The starting point for the simulations is a three layer CIGS model discussed earlier [15], with an additional mid-gap recombination center being present in the absorber. This baseline configuration includes a 200-nm ZnO window,

50-nm CdS buffer, and 3-μm CIGS absorber layer. The uniform Ga-content device efficiency with these parameters is shown as a function of the absorber-band gap in Fig. 1; $\eta(E_g = 1.04 \text{ eV}) = 15.1\%$ and $\eta(E_g = 1.15 \text{ eV}) = 16.8\%$, which is typical for good CIS and ungraded CIGS solar cells. Recombination at the CdS/CIGS interface is not included since earlier calculations have shown that for positive band offsets, interface recombination has a negligible effect [16]. For all cases considered here this criteria is fulfilled. A standard terrestial AM1.5 spectrum is used for the simulated illumination [17].

Band-gap variations (front, back, and double gradings) are described in this paper by the parameters ΔE_{Fr} (linear E_g-increase towards the front), ΔE_{Ba} (linear E_g-increase towards the back), E_{min} (minimum band gap), and d_{min} (distance of the minimum from the junction). The numerical model approximates the linear variations by discrete layers of varying band gap and optical absorption spectrum. The band-gap difference between two adjacent layers is always less than 2kT and in most cases less than kT (26 meV). Hence, a graded device model typically consists of $10 - 25$ layers of absorber material. The absorption spectrum used is that reported for 1.15 eV CIGS [18], and it is shifted on the energy axis according to the band-gap in each layer.

3   Results

3.1   Back grading

Back grading establishes an additional drift field for the minority electrons that assists carrier collection and reduces back contact recombination. Normalized current-voltage parameters for $E_{min} = 1.04$ eV, $\Delta E_{Ba} = 0 - 0.6$ eV, and d_{min}

$= 0.1 - 2.5$ μm are shown in Fig. 2. Normalization is achieved by studying the difference in short circuit current density ΔJ_{sc}, fill factor ΔFF, and efficiency $\Delta \eta$ between graded and ungraded absorber devices with the same open-circuit voltage ($\Delta V_{oc} = 0$).

A small J_{sc} increase is observed once the back grading extends into the front half of the device ($d_{min} < 1.5$ μm). The improvement is about $1 - 1.5$ mA/cm^2 and weakly dependent on the parameter ΔE_{Ba}. FF shows a negligible decrease with large ΔE_{Ba} and small d_{min}. The net gain in efficiency is typically 0.5%. With $\Delta E_{Ba} > 0.4$ eV and $d_{min} \approx 0.3$ μm, we observe a maximum $\Delta \eta = 0.7\%$.

3.2 Thin CIGS absorbers

Material as well as deposition costs can be greatly reduced by thinning the absorber layers from the standard thickness of $2 - 3$ μm. Optically, less than 0.5 μm is needed to absorb more than 90% of the light with $E_{ph} > E_g$, even without considering reflection of the light at the back contact. Lundberg et al. [19] investigated the performance of CIGS solar cells as a function of absorber thickness and found that the dominanting loss for thinner absorber layers is a reduction of J_{sc}, which exceeds the reduction in generation due to increased back contact recombination.

Predicted efficiencies for the constant band-gap model with a reduced absorber thickness of 0.5 μm are shown in Fig. 1. Efficiency is lowered by about 2%, and these losses are mostly in J_{sc}, followed by a lower FF, and a slightly reduced V_{oc}. Experimentally, an efficiency loss closer to 6% has been observed for 0.5 μm CIGS [19]. This larger loss is most likely correlated to the experi-

mental difficulties in adjusting the film thickness without changing other film parameters at the same time, especially morphology and defect structure.

When a thin CIGS absorber of 0.5 μm is simulated without consideration of material-quality changes, the effects of back contact passivation can be highlighted. Such results are shown in Fig. 3. The model predicts that J_{sc} losses can be fully recovered by a fairly steep back grading and, hence, absorber thinning is predicted to be practical without significant loss in efficiency.

3.3 Double grading

Conceptually, double grading allows increased performance by achieving a high J_{sc}, which is determined by the minimum band-gap in the device, and at the same time increased V_{oc} due to the locally increased band gap in the space-charge region. This principal of two band gaps was experimentally verified by Dullweber et al. [20]. The quantified η gains, reported in [10], however, used the minimum band-gap absorber as reference performance and overestimated the grading effect.

The *normalized* current-voltage parameters from our simulations, for E_{min} = 1.04 eV, ΔE_{Ba} = 0 − 0.6 eV, $\Delta E_{Ba}/\Delta E_{Fr}$ = 2, and d_{min} = 0.1 − 2.5 μm, show that the double grading benefits are rather modest (Fig. 4). For d_{min} < 0.3 μm the simulations predict J_{sc} gains similar to those with the back grading. For larger d_{min}, however, J_{sc} is strongly reduced, as much as 5 mA/cm^2, depending on the height of ΔE_{Fr}. FF improves with small d_{min}, but it also shows considerable reduction for intermediate $d_{min} \approx 0.2 − 1.5$ μm. The highest efficiency gain should be close to 1% when the minimum band gap is

6

located in the middle of the space charge region near 0.2 μm. Comparing this 1% increase with the 0.7% achieved by back grading alone, the gain achieved by the separation of electrical and optical band-gap is quite modest. Models in which only a front grading were implemented show similar losses in J_{sc} and FF, and under no circumstances was an efficiency gain observed.

3.4 Current-loss explanation

The losses in J_{sc} for intermediate values of d_{min} result approximately equally from the reduced absorption in the junction region and from the poorer collection due to the reduction and possible reversal of the drift field for minority carriers. Fig. 5 shows the conduction band for three different front gradings with d_{min} = 0.1, 0.3, and 1 μm under zero bias (b) and at a voltage between the maximum power voltage and V_{oc} (a). For small d_{min} the front grading is completely contained in the space charge region and slightly reduces the field. With d_{min} = 0.3 μm good collection is still possible at zero voltage (no reduction in J_{sc}). However, a barrier exists under forward bias that leads to poorer collection and is observed as a reduction in the FF. Larger values for d_{min} lead to barriers under all condition, reducing J_{sc} and FF. For materials with lower carrier concentrations (here we used $2\text{x}10^{16}$ cm^{-3} for the CIGS layer), the range of d_{min} that is unfavorable is expected to decrease.

4 Discussion and Conclusions

Back grading in CIGS solar cells is seen to improve simulated device efficiency compared to ungraded devices. For devices with standard thicknesses, the

effect is small, around 0.5% in efficiency. The potential efficiency gain increases significantly as the absorber thickness is reduced. We predict $\Delta\eta \approx +2\%$ with a thickness of 0.5 μm, which means that the thinning losses are fully recovered. These efficiency gains are in good agreement with experimental work [13], but experimentally the thinning losses were greater and not fully recovered by adding back grading.

Double grading shows benefits similar to those from back grading, but the additional front grading can lead to large losses in FF and J_{sc}, if the band-gap minimum is not contained within the space charge region. The large FF loss has been observed by Topic et al. [3] and was argued to be due to the reverse drift field for the minority carriers. Our simulations confirm this conclusion.

With larger minimum band-gap energies of 1.2 eV (instead of 1.04 eV), slightly higher gains up to $\Delta\eta = 1.2\%$ are achieved, and the highest absolute efficiency of 18.6% exceeds the highest uniform band gap efficiency by 0.6%. Higher ratios $r = \Delta E_{Ba}/\Delta E_{Fr}$ also seem to be favorable: the highest efficiency gain ($E_{min} = 1.04$ eV) increased from 0.6% for the $r = 1$, 1% for $r = 2$, and 1.2% for $r = 3$.

Although frequently believed to be a major contributor to high efficiency devices, we have shown that the benefit that can be expected by implementing back, front, or double grading in standard-thickness CIGS solar cells to be small. Large losses in FF and J_{sc} can be realized with front and double gradings. Thin CIGS devices, however, can benefit significantly from a back grading that reduces back contact recombination.

5 Acknowledgments

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Figure Captions

Figure 1: (a) Simulated device efficiency, η, and open-circuit voltage, V_{oc}, for CIGS solar cells with uniform band-gap energies and thicknesses of 3 μm (solid) and 0.5 μm (dashed).

Figure 2: Change in J_{sc}(a), FF (b), and η (c) due to the addition of back grading in "thick" (3 μm) CIGS devices. The numbers shown are the differences to results found with uniform band-gap energies of equal V_{oc}.

Figure 3: Change in J_{sc}(a), FF (b), and η (c) due to the addition of back grading in thin (0.5 μm) CIGS devices.

Figure 4: Change in J_{sc}(a), FF (b), and η (c) due to the addition of double grading. E_g increases by ΔE_{Fr} towards the front and by ΔE_{Ba} towards the back of the device.

Figure 5: Conduction band energy at zero voltage and under forward bias. Intermediate positions of the band-gap minimum lead to a significant reverse field for electrons.
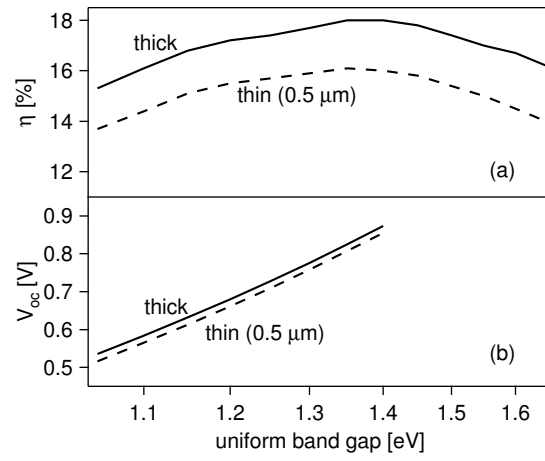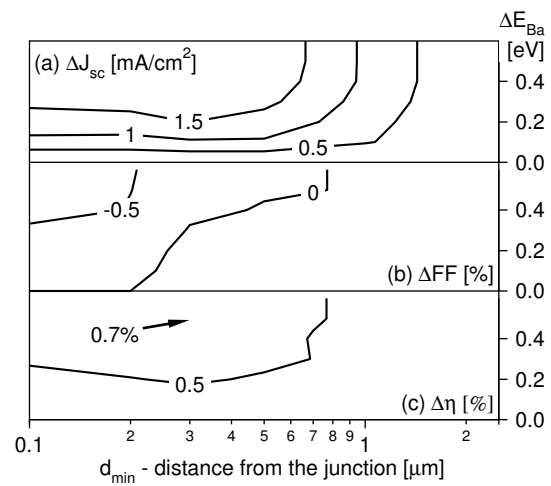
Figure 1

Figure 2

(a) ΔJ_{sc} [mA/cm^2]

ΔE_{Ba} [eV]

4

3

2

1

(b) ΔFF [%]

-1
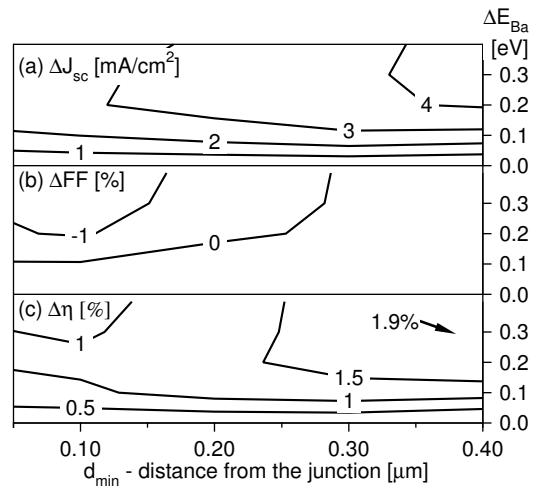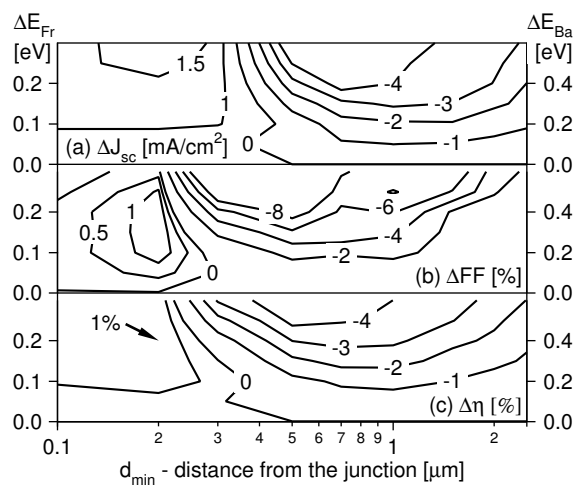
0

(c) $\Delta \eta$ [%]

1

1.9%

1.5

1

0.5

d_{min} - distance from the junction [μm]

Figure 3

Figure 4

Figure 5